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Europäisches Patentamt
European Patent Office
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(11) Publication number:

**0 326 632
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 88101478.1

(51) Int. Cl. 4: C08J 5/22

(22) Date of filing: 02.02.88

(43) Date of publication of application:
09.08.89 Bulletin 89/32

(84) Designated Contracting States:
BE DE FR GB IT NL

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(54) Method for the preparation of perfluorosulfonate ionomer films.

(57) The invention is a method for forming a perfluorosulfonate ionomer film comprising:

- (a) forming a solution of a perfluorosulfonate ionomer in its salt form,
- (b) coating a substrate with the perfluorosulfonate ionomer solution, and
- (c) heating the coated substrate to a temperature of at least about 120° C to deposit a solvent-resistant film of a perfluorosulfonate ionomer onto the substrate.

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METHOD FOR THE PREPARATION OF PERFLUOROSULFONATE IONOMER FILMS

Perfluorosulfonate ionomers (PFSI's) such as E. I. duPont de Nemours & Co.'s Nafion polymer, are proving to be versatile membrane materials in a variety of applications. For example, PFSI's have been used in electrochemical processes and devices including chloralkali cells, batteries, fuel cells, and water electrolyzers. However, many applications require PFSI's to be formed into films. This is frequently accomplished through dissolving the PFSI in a solvent, depositing the solution onto a substrate, and removing the solvent. High-temperature, high-pressure procedures for dissolving PFSI membranes have recently been reported in U.S. Patent 4,433,082 and in an article by C. R. Martin, T. A. Rhoades, and J. A. Ferguson, *Anal. Chem.*, 1982, 54, 1639. Using such procedures, solutions of PFSI have been formed and used to prepare PFSI-coated electrodes, catalysts and high performance liquid chromatography packing materials. However, such methods do not produce a film that is entirely satisfactory because its properties are different from the polymer before it was formed into a film.

Any film-forming method used with PFSI's preferably should produce PFSI films which possess the solubility behavior, chemical, mechanical and thermal stability equivalent to the PFSI material as it was originally produced. For example, films formed by prior art methods, such as those discussed above, are easily dissolved in an ethanol/water mixture, while the original polymer was not so easily dissolved. In addition, the PFSI's cluster-channel morphology is changed when the polymer is formed into a film. The cluster-channel morphology is important because it helps to impede anion transport, which is a desirable property if these films are to accomplish the task for which they are being used, i.e., to reject anions. The present invention provides a method which can be used to produce films having properties similar to those of the polymer before they were formed into the film.

References which teach dissolving a PFSI in a high boiling point solvent include: "Electrochemical, IR and XPS Study of Nafion Films Prepared From Hexamethylphosphotriamide Solution," *Journal of Electroanalytical Chemistry*, Volume 199 (1986), pages 81-82; "Study of Nafion Films On Electrodes Prepared From Dimethylacetamide Solution," *Journal of Electroanalytical Chemistry*, Volume 200 (1986), pages 379-381; and United States Patent No. 4,433,082, "Process For Making Liquid Composition of Perfluorinated Ion Exchange Polymer, and Product Thereof," W. G. Grot.

More particularly, the invention resides in a

method for forming a perfluorosulfonate ionomer film comprising:

(a) forming a solution of a perfluorosulfonate ionomer in its salt form,

(b) coating a substrate with the perfluorosulfonate ionomer solution, and

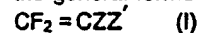
(c) heating the coated substrate to a temperature of at least about 120° C to deposit a solvent-resistant film of a perfluorosulfonate ionomer onto the substrate.

The term "solvent-resistant film" means a film which, after being contacted with a 50:50 volume ratio of an ethanol:water solution at 50° C for one hour in an ultrasonic bath and dried is found to have lost less than 8 percent of its weight, and preferably less than 5 percent of its weight.

Perfluorosulfonate ionomers (PFSI) like those described in the following patents are suitable for use in the present invention: 3,282,875; 3,909,378; 4,025,405; 4,065,366; 4,116,888; 4,123,336; 4,126,588; 4,151,052; 4,176,215; 4,178,218; 4,192,725; 4,209,635; 4,212,713; 4,251,333; 4,270,996; 4,329,435; 4,330,654; 4,337,137; 4,337,211; 4,340,680; 4,357,218; 4,358,412; 4,358,545; 4,417,969; 4,462,877; 4,470,889; and 4,478,695; European Patent Application 0,027,009. Such PFSI's usually have equivalent weight in the range of from 500 to 2000.

Particularly preferred for use in the present invention are PFSI's containing repeating units formed from the polymerization of monomer I with monomer II (as defined below). Optionally, repeating units can be formed from the inclusion of a third type of monomer during the polymerization of monomer I and monomer II.

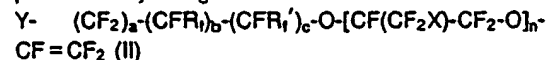
The first type of monomer is represented by the general formula:



where:

Z and Z' are independently selected from -H, -Cl, -F, or -CF₃.

The second type of monomer consists of one or more monomers selected from compounds represented by the general formula:



where:

Y is selected from -SO₂OA where:

A is selected from -H⁺, an alkali metal, or

-R₁R₂R₃R₄N⁺; and where R₁, R₂, R₃, and R₄ are independently selected from -H⁺, a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

a is 0-6;

b is 0-6;

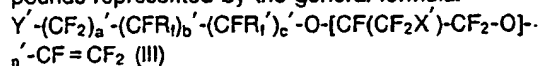
c is 0 or 1;
 provided $a + b + c$ is not equal to 0;
 X is selected from -Cl, -Br, -F, or mixtures thereof
 when $n > 1$;
 n is 0 to 6; and R_1 and R_1' are independently
 selected from -F, -Cl, perfluoroalkyl radicals having
 from 1 to 10 carbon atoms and fluorochloroalkyl
 radicals having from 1 to 10 carbon atoms.

Particularly preferred as a PFSI for use in the
 present invention is a polymer having repeating
 units formed from the monomers shown above
 where $n = 0$ or 1; R_1 and R_1' is -F; X is -Cl or -F;
 and $a + b + c$ is equal to 2 or 3.

Where A is $-H^+$, it is desirable to convert A to
 its salt form by reacting it with an appropriate base,
 e.g. sodium hydroxide or potassium hydroxide.
 Preferably, A is converted to an alkali metal, par-
 ticularly $-ONa^+$ or $-OK^+$ by reacting the PFSI with a
 sodium hydroxide or potassium hydroxide aqueous
 solution, respectively. Such conversions are well
 known to those skilled in the art.

It has been discovered that the H^+ -form PFSI's
 tend to char when heated to temperatures above
 $120^\circ C$, thus the hydrogen form of a PFSI degrades
 during the removal of the solvent.

The third repeating unit which may optionally
 be present in the polymer may be an unsaturated
 perfluoroalkyl monomer other than those represent-
 ed by the general formula II, above. Particularly
 preferred is a repeating unit selected from com-
 pounds represented by the general formula:



where:

Y' is selected from -F, -Cl or -Br;

a' and b' are independently 0-3;

c is 0 or 1;

provided $a + b' + c'$ is not equal to 0;

n' is 0-6;

R_1 and R_1' are independently selected from -Br, -Cl,
 -F, perfluoroalkyl radicals having from 1 to 10 car-
 bon atoms, and chloroperfluoroalkyl radicals having
 from 1 to 10 carbon atoms; and

X' is selected from -F, -Cl, -Br, or mixtures thereof
 when $n' > 1$.

Forming a solution of a PFSI in its salt form
 may be accomplished by contacting the PFSI with
 one or more of a particular group of solvents.
 Solvents which are useful in the present invention
 include solvents having a boiling point above
 $120^\circ C$ and a solubility parameter in the range of
 from 10 to 16. Preferably, the solvent is a polar
 aprotic solvent such as N,N'-dimethylformamide
 (DMF), dimethyl-sulfoxide (DMSO), N-methyl pyr-
 rolidone, tetramethyl urea, triphenylphosphate,
 dimethylacetamide, sulfolane, butyrolactone, and
 the like. In addition, ethylene glycol may be used
 as the solvent, although it is not preferred because

very high evaporating temperatures are required
 and they tend to decompose the polymer. It has
 been discovered that the use of water to enhance
 the dissolution of the PFSI is unnecessary for the
 redissolution of the PFSI using the solvent, al-
 though it may, optionally, be used.

The dissolution can be conducted at ambient
 temperature and pressure, although elevated tem-
 peratures and pressures may, optionally, be used.
 Stirring or agitation in an ultrasonic bath may be
 used to enhance the rate of dissolution. The par-
 ticular temperature and the time used to dissolve
 the PFSI in the second solvent is not critical to the
 successful practice of the invention.

Typically, the PFSI solutions formed according
 to the procedure of the present invention have a
 weight/volume percent (w/v %) of from 0.01 to 8
 percent by weight of PFSI. Preferably, the per-
 fluorosulfonate ionomer in the solution has a con-
 centration of from 0.5 to 3 w/v %. However, for the
 formation of films according to the present inven-
 tion, the actual concentration of the PFSI in the
 solution is not critical. Although it might be neces-
 sary, when working with low-concentration solu-
 tions, to use more than one coating of the solution
 on the substrate to form a continuous film. How-
 ever, if non-continuous films are acceptable, a one-
 coat layer of the solution might be sufficient.

Along with the solvents listed above, it is ac-
 ceptable to use co-solvents. The solvent/co-solvent
 mixture must, however, be able to solvate the ionic
 portion of the PFSI, while plasticizing the non-ionic
 (fluorocarbon) portion of the PFSI, if a good film is
 to be formed. The co-solvent can contribute to
 either of these functions. Materials suitable for use
 as a co-solvent are one or more solvents selected
 from the group consisting of C_1 to C_{12} alcohols, 2-
 methoxyethanol, 2-ethoxyethanol, ethylene glycol
 dimethyl ether, ethylene glycol diethyl ether,
 diethylene glycol dimethyl ether, diethylene glycol
 diethyl ether, dioxane, and acetonitrile.

After dissolving the PFSI in the solvent or the
 solvent/co-solvent mixture to form a solution, the
 solution is contacted with the substrate upon which
 it is desired to have a PFSI film deposited. The
 solution may be coated onto the substrate by dip-
 ping the substrate into the solution, by painting or
 spraying the solution onto the substrate, or by a
 variety of other processes well-known in the art.

The substrate itself can be any of a wide
 variety of materials, including a fabric (especially a
 fabric made at least in part of perhalocarbon fibers
 or glass fibers), an ion exchange membrane, or a
 porous diaphragm, in this latter case for the pur-
 pose of converting the porous diaphragm to a
 nonporous membrane-like article. The coated arti-
 cles so made can be used in various liquid perme-
 ation processes, such as reverse osmosis, ultrafil-

tration, and electrolysis, especially electrolysis of aqueous sodium chloride solution.

The solution can also be used to coat catalyst supports, such as metals or ceramics. Such catalysts are useful in catalyzing alkylations, ether formations, and a host of other acid catalyzed chemical reactions. Other substrates are described in U. S. Patent No. 4,277,344, "Interfacially Synthesized Reverse Osmosis Membrane." There, a variety of organic polymeric materials are used as substrates, including polysulfone, chlorinated polyvinyl chloride, polyvinyl butyral, polystyrene, and cellulose esters. The substrate can be microporous so as to have millions of pores per square centimeter. Typical pore sizes range from 1 to 1000 millimicrons in their widest dimension.

After the solution has been coated onto the desired substrate, the solvent or solvent/co-solvent mixture is removed from the solution, thereby precipitating the PFSI onto the substrate. However, it has been discovered that solvent-resistant films are formed only when the solvent is removed from the solution by heating the solution to temperatures greater than 120°C.

It has further been discovered that the higher the solubility parameter of the solvent, the higher the processing temperature should be for removing the solvent. For example, when DMF is used as the solvent, it is optimal to heat the solution to a temperature range of from 120°C to 165°C for the removal of the DMF. Most preferably, the DMF is removed at a temperature of about 165°C. DMF has a solubility parameter of 12.1 Hildebrands (Hb). Likewise, when DMSO is used as the solvent, it is optimal to heat the solution to a temperature range of from 165°C to 185°C for removal of the DMSO. DMSO has a solubility parameter of 12.9 Hb. Similarly, when ethylene glycol is used as the solvent, it is optimal to heat the solution to a temperature range of from 180°C to 190°C. Ethylene glycol has a solubility parameter of 16.3 Hb.

It is a further feature of the invention that a portion of the solvent from the coating solution on the substrate can be removed at moderate temperatures with reduced pressures, provided such preliminary drying is followed by sufficient drying at elevated temperatures to produce a solvent resistant film.

Although the reasons for the formation of films having properties similar to the polymers as originally produced is not entirely understood, it is thought that it is related to the amount of crystallinity and to the formation of ionic clusters in the PFSI. Films which show poor physical and mechanical characteristics have been found to show distinctly different x-ray scattering spectra than both films prepared according to the present invention and PFSI films obtained from hydrolysis of the

thermoplastic precursors.

Example 1

This example shows the use of the invention on an PFSI using dimethylsulfoxide as the solvent.

A 0.5 gram sample of a sulfonic acid type PFSI in its proton form having an equivalent weight of about 1286 was contacted with about 89.3 grams of a 50:50 ethanol:water mixture at a temperature of about 250°C at a pressure of about 800 pounds per square inch (5512 kPa) to dissolve the PFSI, thereby forming a first solution. The PFSI solution was then filtered through a Whatman #1 paper filter to remove any undissolved polymer. This produced a solution having a 0.445 weight/volume percent.

The solution was then neutralized by adding about 8.1 grams of a 0.05 Molar NaOH solution to convert the PFSI into its sodium form. It was then heated to about 60°C and maintained at that temperature for a time sufficient for the solvent to substantially completely evaporate, thereby forming a brittle film. The PFSI film was then removed and ground at room temperature into a fine white powder.

The method of the present invention was then used to form the polymer into a film. A 50 milligram sample of the PFSI powder prepared above was added to 10 milliliters of DMSO and then agitated in an ultrasonic bath for about 30 minutes to promote dissolution of the polymer. The temperature of the PFSI solution rose to about 40°C during this procedure.

The DMSO was then substantially completely evaporated at a temperature of about 185°C leaving the PFSI behind in the form of a film in the evaporation container. The PFSI film was clear, pliant, mechanically stable and could be removed from the walls of the evaporation vial as a coherent membrane.

The solubility of the PFSI film was assessed quantitatively by immersion of the solution processed film in 10 milliliters of a 50:50 ethanol:water solution with agitation from an ultrasonic bath for 1 hour. (Ultrasonication caused the temperature of the ethanol:water solvent to rise to about 50°C.) The solvent was then filtered through a Whatman #1 filter and evaporated to dryness. The solid residue was weighed and the percent (w/v) of the solution processed PFSI which was soluble was calculated to be about 3.5%.

Example 2

This example shows the invention used on Nafion PFSI and using dimethylsulfoxide as the

solvent.

A 0.5 gram sample of a sulfonic acid Nafion perfluorosulfonate ionomer (proton form) having an equivalent weight of about 1100 was contacted with about 89.3 grams of a 50:50 ethanol:water mixture at a temperature of about 250 °C at a pressure of about 800 pounds per square inch (5512 kPa) to dissolve the PFSI, thereby forming a solution. The PFSI solution was then filtered through a Whatman #1 paper filter to remove any undissolved polymer. This produced a 0.428 w/v % solution of the PFSI.

The solution was then neutralized by adding about 7.8 grams of a 0.05 Molar NaOH solution to convert the PFSI into its sodium form. This solution was heated to about 60 °C allowing the solvent to substantially completely evaporate subsequently forming a brittle film. The PFSI was then removed and ground at room temperature into a fine white powder.

The present invention was then used to prepare the PFSI into a film. A 50 milligram sample of the PFSI powder was added to 10 milliliters of DMSO and then agitated in an ultrasonic bath for about 30 minutes to promote dissolution of the polymer. The temperature of the PFSI solution rose to about 40 °C during this procedure.

The DMSO was substantially completely evaporated at a temperature of about 185 °C leaving the PFSI behind in the evaporation container. The PFSI was in the form of a film which was clear, pliant, mechanically stable and could be removed from the walls of the evaporation vial as a coherent film. The solubility of the PFSI film was assessed quantitatively by immersion of the solution processed film in 10 milliliters of a 50:50 ethanol:water solution with agitation from an ultrasonic bath for 1 hour. (Ultrasonication caused the temperature of the ethanol:water solvent to rise to about 50 °C.) The solution was then filtered through a Whatman #1 filter and evaporated to dryness. The solid residue was weighed and the solute was found to be about 1.4% soluble.

Example 3

This example shows the invention used on Nafion PFSI and using dimethylformamide as the solvent.

A 0.5 gram sample of a sulfonic acid Nafion perfluorosulfonate ionomer (proton form) having an equivalent weight of about 1100 was contacted with about 89.3 grams of a 50:50 ethanol:water mixture at a temperature of about 250 °C at a pressure of about 800 pounds per square inch (5512 kPa) to dissolve the PFSI, thereby forming a first solution. The PFSI solution was then filtered through a Whatman #1 paper filter to remove any undissol-

ved polymer. This produced a 0.428 w/v % solution of the PFSI.

The solution was then neutralized by adding about 7.8 grams of a 0.05 Molar NaOH solution to convert the PFSI into its sodium form. This solution was heated to about 60 °C allowing the solvent to completely evaporate subsequently forming a brittle film. The PFSI was then removed and ground at room temperature into a fine white powder.

The film was then used according to the method of the present invention to form a film. A 50 milligram sample of the PFSI powder was added to 10 milliliters of DMF and then agitated in an ultrasonic bath for about 30 minutes to promote dissolution of the polymer. The temperature of the PFSI solution rose to about 40 °C during this procedure.

The DMF was completely evaporated at a temperature of about 165 °C leaving the PFSI behind in an evaporation container. The PFSI was in the form of a film which was clear, pliant, mechanically stable and could be removed from the walls of the evaporation vial as a coherent film. The solubility of the PFSI film was assessed quantitatively by immersion of the solution processed film in 10 milliliters of a 50:50 ethanol:water solution with agitation from an ultrasonic bath for 1 hour. (Ultrasonication caused the temperature of the ethanol:water solvent to rise to about 50 °C.) The solvent was then filtered through a Whatman #1 filter and evaporated to dryness. The solid residue was weighed and the PFSI was found to be about 3.8% soluble.

Example 4

This example shows the invention used on Nafion PFSI and using ethylene glycol as the solvent.

A 0.5 gram sample of a sulfonic acid Nafion perfluorosulfonate ionomer (proton form) having an equivalent weight of about 1100 was contacted with about 89.3 grams of a 50:50 ethanol:water mixture at a temperature of about 250 °C at a pressure of about 800 pounds per square inch (5512 kPa) to dissolve the PFSI, thereby forming a solution. The PFSI solution was then filtered through a Whatman #1 paper filter to remove any undissolved polymer. This produced a 0.428 w/v % solution of the PFSI.

The solution was then neutralized by adding about 7.8 grams of a 0.05 Molar NaOH solution to convert the PFSI into its sodium form. This solution was heated to about 60 °C allowing the solvent to completely evaporate subsequently forming a brittle film. The PFSI was then removed and ground at room temperature into a fine white powder.

The PFSI was then used in the method of the present invention to form a film. A 50 milligram

sample of the PFSI powder was added to 10 milliliters of ethylene glycol and then agitated in an ultrasonic bath for about 30 minutes to promote dissolution of the polymer. The temperature of the PFSI solution rose to about 40°C during this procedure.

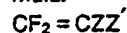
The ethylene glycol was completely evaporated at a temperature of about 185°C leaving the PFSI behind. The PFSI was in the form of a film which was clear, pliant, mechanically stable and could be removed from the walls of the evaporation vial as a coherent film. The solubility of the PFSI film was assessed quantitatively by immersion of the solution processed film in 10 milliliters of a 50:50 ethanol:water solution with agitation from an ultrasonic bath for 1 hour. (Ultrasonication caused the temperature of the ethanol:water solvent to rise to about 50°C.) The solvent was then filtered through a Whatman #1 filter and evaporated to dryness. The solid residue was weighed and the PFSI was determined to be about 6.5% soluble.

Claims

1. A method for forming a perfluorosulfonate ionomer film comprising:

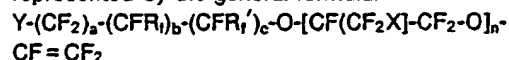
- (a) forming a solution of a perfluorosulfonate ionomer in its salt form,
- (b) coating a substrate with the perfluorosulfonate ionomer solution, and
- (c) heating the coated substrate to a temperature of at least about 120°C to deposit a solvent-resistant film of a perfluorosulfonate ionomer onto the substrate.

2. The method of Claim 1, wherein the perfluorosulfonate ionomer is a copolymer of a first repeating unit selected from a first group of monomers and a second repeating unit selected from a second group of monomers wherein the first group of monomers is represented by the general formula:



where:

Z and Z' are independently selected from -H, -Cl, -F, or -CF₃; and the second group of monomers is represented by the general formula:



where:

Y is selected from -SO₂OA where:

A is selected from -H, an alkali metal, or -R₁ R₂ R₃ R₄ N; and where R₁, R₂, R₃, and R₄ are independently selected from -H, a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

a is 0-6;

b is 0-6;

c is 0 or 1;

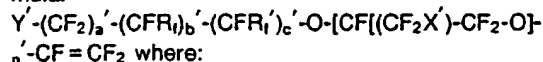
provided a + b + c is not equal to 0;

X is selected from -Cl, -Br, -F, or mixtures thereof when n > 1;

n is 0 to 6; and

R₁ and R₁' are independently selected from -F, -Cl, perfluoroalkyl radicals having from 1 to 10 carbon atoms and fluorochloroalkyl radicals having from 1 to 10 carbon atoms.

3. The method of Claim 2, including a third type of monomer represented by the general formula:



where:

Y' is selected from -F, -Cl or -Br;

a' and b' are independently 0-3;

c is 0 or 1;

provided a' + b' + c' is not equal to 0;

n' is 0-6;

R₁ and R₁' are independently selected from -Br, -Cl, -F, perfluoroalkyl radicals having from 1 to 10 carbon atoms, and chloroperfluoroalkyl radicals having from 1 to 10 carbon atoms; and

X' is selected from -F, -Cl, -Br, or mixtures thereof when n' > 1.

4. The method of Claim 2, wherein n = 0 or 1; R₁ and R₁' are -F; X is -Cl or -F; and a + b + c is equal to 2 or 3.

5. The method of Claim 1, wherein the solution includes a solvent selected from N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-methyl pyrrolidone, triphenylphosphate, tetramethyl urea, dimethyl-acetamide, sulfolane, butyrolactone and ethylene glycol.

6. The method of Claim 5, wherein the solvent includes water.

7. The method of Claim 1, wherein the perfluorosulfonate ionomer in the solution has a concentration of from 0.01 to 8 weight/volume percent.

8. The method of Claim 1, wherein the perfluorosulfonate ionomer in the solution has a concentration of from 0.5 to 3 weight/volume percent.

9. The method of Claim 5 or 6, wherein the solution includes a co-solvent selected from C₁ to C₁₂ alcohols, 2-methoxyethanol, 2-ethoxyethanol, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, dioxane, and acetonitrile.

10. The method of Claim 1, wherein the substrate is selected from wire mesh, ceramics, cloth fabrics, ion exchange membranes and porous diaphragms.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 10 1478

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
P,X	US-A-4 731 263 (C.R. MARTIN et al.) * Whole document *	1-10	C 08 J 5/22

X	FR-A-2 024 289 (E.I. DU PONT DE NEMOURS) * Claims; page 4, lines 30-33; page 2, lines 1-19 *	1-10	

D,X	EP-A-0 066 369 (E.I. DU PONT DE NEMOURS) * Claims *	1-10	

X	US-A-4 650 551 (W.P. CARL et al.) * Claims; column 2, lines 45-49; column 3 *	1-4	

A	US-A-4 298 697 (S.K. BACZEK et al.)		

D,A	EP-A-0 041 732 (DOW)		

D,A	EP-A-0 041 733 (DOW)		

The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30-09-1988	Examiner VAN GOETHEM G.A.J.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	